

Scotland's Rural College

Isolating the effect of soil properties on agricultural soil greenhouse gas emissions under controlled conditions

Miller, G A; Rees, RM; Griffiths, BS; Cloy, JM

Published in:
Soil Use and Management

DOI:
[10.1111/sum.12552](https://doi.org/10.1111/sum.12552)

Print publication: 01/04/2020

Document Version
Peer reviewed version

[Link to publication](#)

Citation for pulished version (APA):

Miller, G. A., Rees, RM., Griffiths, BS., & Cloy, JM. (2020). Isolating the effect of soil properties on agricultural soil greenhouse gas emissions under controlled conditions. *Soil Use and Management*, 36(2), 285-298.
<https://doi.org/10.1111/sum.12552>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

1 **Isolating the effect of soil properties on agricultural soil greenhouse gas emissions under**
2 **controlled conditions**

3 Gemma A. Miller^{a*}, Robert M. Rees^a, Bryan S. Griffiths^a and Joanna M. Cloy^a

4 ^a Scotland's Rural College, West Mains Road, Edinburgh, EH9 3JG, UK.

5 * Corresponding author: gemma.miller@sruc.ac.uk

6

Abstract

Agricultural soils are important sources of greenhouse gases (GHGs). Soil properties and environmental factors have complex interactions which influence the dynamics of these GHG fluxes. Four arable and five grassland soils which represent the range of soil textures and climatic conditions of the main agricultural areas in the UK were incubated at two different moisture contents (50 or 80 % water holding capacity) and with or without inorganic fertiliser application (70 kg N ha⁻¹ ammonium nitrate) over 22 days. Emissions of N₂O, CO₂ and CH₄ were measured twice per week by headspace gas sampling and cumulative fluxes were calculated. Multiple regression modelling was carried out to determine which factors (soil mineral N, organic carbon and total nitrogen contents, C:N ratios, clay contents and pH) that best explained the variation in GHG fluxes. Clay, mineral N and soil C contents were found to be the most important explanatory variables controlling GHG fluxes in this study. However, none of the measured variables explained a significant amount of variation in CO₂ fluxes from the arable soils. The results were generally consistent with previously published work. However, N₂O emissions from the two Scottish soils were substantially more sensitive to inorganic N fertilisation at 80% water holding capacity than the other soils, with the N₂O emissions being up to 107 times higher than the other studied soils.

Keywords: GHG emissions, inorganic fertiliser, agricultural soils

Running head: Agricultural soil greenhouse gas emissions

1 Introduction

Agricultural soils are important sources of atmospheric greenhouse gases (GHGs). Various soil properties, environmental factors and management practices have complex interactions which influence the dynamics of these GHG fluxes. Soil texture is a particularly important factor as it dictates soil water dynamics, pore space and gas diffusivity (Skiba & Ball 2002). The availability of nitrogen (N) for microbial processes is also an influential factor (Cardenas *et al.* 2019).

Greenhouse gas fluxes from agricultural soils are influenced by environmental factors such as temperature, precipitation, and soil physical and chemical properties such as texture, pH, oxygen concentration and nutrient availability. Texture affects pore space distribution and gas diffusivity (Smith *et al.*, 2003) whilst soil pH manipulates the microbial community structure, and therefore the decomposition or accumulation of soil organic carbon (SOC) (Malik *et al.*, 2018). The soil texture, particularly the clay content, determines the level of physico-chemical stabilisation of SOC through association with soil minerals (Schrumpf *et al.*, 2013). Soil wetness strongly influences soil GHG emissions. Production of N₂O by nitrification increases linearly as increasing soil water content approaches 60% of water filled pore space (WFPS). At higher water contents denitrification becomes more prevalent leading to maximum emissions at around 80% WFPS (Shepherd, 2009). Soil CO₂ emissions decrease substantially after heavy rainfall because poor gas diffusivity and low air-filled porosity restrict respiration and increase anaerobic conditions (Ball, 2013). Anaerobic soil conditions can promote the production of CH₄ via methanogenesis whilst methanotrophy (CH₄ oxidation to CO₂) is more prominent in aerated soils allowing diffusion of CH₄ into the soil from the atmosphere (Cloy and Smith, 2015). In fine textured soils, pore spaces are smaller and so a lower volume of water is required to reach the same WFPS as in a coarser textured soil. Limited diffusion in fine textured soils therefore tends to support the development of anaerobic microsites and so tend to emit more N₂O than coarser textured soils (Stehfest and Bouwmann, 2006).

Application of inorganic N such as ammonium nitrate (AN) fertiliser to soil temporarily creates an excess of available-N required for microbial nitrification and denitrification (NH₄⁺ and NO₃⁻, respectively) which reduces microbial competition for these resources (Norton and Firestone, 1996).

The application of inorganic N may also decrease or reverse the soil's CH₄ sink and source capacity (Inselsbacher *et al.*, 2011).

Across the UK, GHG emissions from agricultural soils vary widely as a consequence of climate, management and soil type. The objective of this study was to isolate the effect of soil chemical and physical properties on GHG emissions by measuring GHG fluxes from soils in a controlled environment. Soils were subjected to two different moisture contents with or without AN application.

2 Materials and Methods

2.1 Soils

Soils were collected from nine UK Agricultural Greenhouse Gas Research Platform sites: four arable (Boxworth, Gilchriston, Rosemaund and Woburn) and five grassland (Crichton, Drayton, Hillsborough, North Wyke and Pwllpeiran). The soils did not receive any N inputs from the end of the 2010 growing season to collection (February to early March 2011, McGeough *et al.*, 2016). Soils were sieved to < 4 mm to remove large stones and roots, air dried and stored in sealed plastic bags. These sites represent the different soil types and climates of the main agricultural areas across the UK (Table 1).

2.2 Treatments

A fully-factorial experiment was designed with two water holding capacities (WHCs) (50% and 80%), and two AN application levels (0 or 70 kg N ha⁻¹). The method of Howard and Howard (1993) and the following equation were used to determine WHC:

$$100\% \text{ WHC} = \frac{\text{mass saturated soil} - \text{mass oven dry soil}}{\text{mass oven dry soil}}$$

Treatments were applied in triplicate to 80 g of soil at a bulk density of ~1 g cm⁻³ (average value found from field measurements of these soils: range 0.6–1.6 g cm⁻³), in 500 ml Kilner jars.

Ammonium nitrate was dissolved in the deionised water used to adjust the WHC. Soils were

incubated at 10 °C (average annual temperature for all sites, Table 1) for 22 days, following a three day pre-incubation period.

2.3 Headspace gas sampling

Headspace gas sampling was undertaken twice per week. Gas samples were taken from Kilner jars at the beginning (t0) and end (t1) of a one hour closure period. Before each sampling period, jars were opened for three minutes to allow gas concentrations in the jar to equilibrate with the laboratory air before sealing the lids with both sampling ports open. The jars were flushed three times through one sampling port using a 60 ml syringe before drawing a 30 ml t0 gas sample and injecting it into a 25 ml pre-evacuated vial, after which both ports were closed. After the t0 headspace gas sampling, jars were returned to the incubator and the 30 ml t1 samples were drawn one hour later with one port remaining closed. Between sampling periods jar lids were closed with both ports open to allow free gas exchange whilst limiting moisture loss. Moisture loss was never more than 1%, and so was not deemed to be significant (calculated from mass change of kilner jars from beginning to end of incubation).

2.4 GHG calculations

Gas samples were analysed for N₂O, CO₂ and CH₄ using an Agilent 7890A Gas Chromatograph (GC) fitted with electron capture, flame ionisation and thermal conductivity detectors (Agilent Technologies, Berkshire, UK) and a CTC Analytics COMBI PAL autosampler (CTC Analytics, Hampshire, UK). The GC gas peak area responses were calibrated (calibration curves were linear for CO₂ and CH₄, quadratic for N₂O) using four certified standard gas mixtures (BOC Industrial Gases, UK). Headspace GHG concentrations were used to calculate GHG fluxes per day using linear regression and the ideal gas law (Saggar *et al*, 2008):

$$F = \rho \frac{V}{A} \frac{\Delta C}{\Delta t} \frac{273.15}{T + 273.15}$$

This calculation assumes a linear increase in gas concentration in a known volume over a known period of time, where F = flux, ρ = gas density, V = jar volume, A = jar basal area, Δc = difference

between gas concentrations at t_1 and t_0 , Δt = jar closure time (hours), T = incubation temperature ($^{\circ}\text{C}$).

Cumulative fluxes were calculated using the trapezoidal rule (area under the curve) to interpolate fluxes between sampling days (Hinton *et al*, 2015; Bell *et al* 2015a,b; Bell *et al*, 2016) as follows:

$$\text{Cumulative flux} = (\text{day } x \text{ cumulative flux} + \text{day } y \text{ flux}) + (\text{mean}(\text{day } x \text{ flux} + \text{day } y \text{ flux})) \\ * (\text{day } y - \text{day } x - 1)$$

Emission factors (EFs) define the percentage of applied N fertiliser which is emitted as N_2O .

Emission factors were calculated for N_2O emissions from AN fertilised soils incubated over the 22-day incubation period using the following equation:

$$\text{EF} = \left(\frac{\text{FN}_2\text{O flux (kg N}_2\text{O} - \text{N}) - \text{CN}_2\text{O flux (kg N}_2\text{O} - \text{N})}{N \text{ applied (kg N)}} \right) * 100$$

where FN_2O = cumulative N_2O flux from fertilised soil and CN_2O = cumulative N_2O flux from unfertilised control soil.

Global warming potentials (GWPs) were calculated as CO_2 equivalents ($\text{CO}_2\text{-eq}$) using IPCC (2014) values over a 100-year timescale of 1, 28 and 265 for CO_2 , CH_4 and N_2O respectively.

2.5 Chemical analyses

Pre- and post-incubation soil mineral N concentrations were determined. Soil subsamples were extracted with 2 M KCl (1:2 soil to KCl) within 24 hours of the final headspace gas sampling.

Extracts were analysed for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ using a Skalar San⁺⁺ continuous flow colorimetric autoanalyser (Skalar, York, UK). Colorimetric determination was carried out at wavelengths of 650 nm and 540 nm for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$, respectively, following the methods of Singh *et al* (2011).

Pre-incubation soil subsamples were extracted with deionised water (1:2) and soil solution pH was measured using a calibrated pH electrode (Thermo-Orion, Beverly, MA, USA).

Air dried, ball milled soil samples were combusted and analysed for organic C (OC) and total nitrogen (TN) using a Flash 2000 elemental analyser (Thermo Fisher Scientific, Bremen, Germany).

2.6 Statistical Analyses

Treatment effects (WHC and AN fertilisation) on cumulative GHG fluxes and pre- and post-incubation mineral N contents were determined by two-way ANOVA. Significant differences between EFs of different soils were determined by one-way ANOVA. Multiple linear regressions were used to evaluate the influence of % clay (as a proxy for soil texture), % OC, % TN, C:N, pH and $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ content on arable and grassland soils. Reduced models were determined by backwards selection of the most significant variables. All statistics were carried out using Genstat (15th edition). To more fully satisfy the assumption of normal distribution of the residuals data was log transformed where appropriate and outlying cumulative GHG flux points were removed from the analyses after scrutiny of the residuals.

3 Results

3.1 Soil properties

Ranges of soil properties across grassland soils were as follows: average TN content 0.27–0.77%; average OC content 2.22–12.35%; average clay content 15.0–56.5%; C:N ratio 8.17–15.99 and pH 4.47–6.67. Ranges of soil properties across arable soils were as follows: average TN content 0.09–0.19%; average OC content 0.94–1.90%; average clay content 11–45%; C:N ratio 8.21–13.57 and pH 5.13–7.91. Specific values for each soil are given in Table 1. Average clay contents were taken from McGeough *et al* (2016). These differences in soil properties are due to natural variation in geology, topography and climate.

3.2 GHG fluxes

Global warming potentials ($\text{CO}_2\text{-eq}$) for grassland and arable soils (Table 2) show that the GHG budgets were generally dominated by N_2O and CO_2 fluxes.

3.2.1 N₂O emissions

The Scottish arable and grassland 80% WHC+N treatment soils had substantially higher N₂O emissions than the other soils ($p < 0.05$, Figure 1a,b). The Scottish grassland soil 80% WHC treatment was also significantly higher than other treatments in all soils except one (Pwllpeiran) ($p < 0.05$, Figure 1b).

During the 22-day incubation period N₂O EFs calculated for the arable and grassland soils (Figures 2a, b) were consistently below the IPCC default value of 1%. This was expected since EFs are usually calculated from one year field measurements however, the EFs calculated here are useful for site comparisons. At 50% WHC the EFs were negligible. The Scottish soils had significantly higher EFs ($p < 0.01$) than the other soils at 80% WHC.

The negative EFs observed for Boxworth and Crichton 50% WHC do not indicate uptake of N₂O from the atmosphere, but rather that the emissions from the unfertilised control treatments were greater than from the fertilised treatments. There were no significant differences between emissions from fertilised and unfertilised soils in these cases where negative EFs were observed.

3.2.2 CO₂ fluxes

There was high variability in cumulative CO₂ fluxes between replicates in the grassland and arable soils. For instance, CO₂ fluxes from Crichton soils at 50% WHC were 2760 ± 1450 mg CO₂-C m⁻², Hillsborough soils at 50% WHC+N had fluxes of 945 ± 532 mg CO₂-C m⁻², at 80% WHC Drayton soil had fluxes of 8890 ± 2350 CO₂-C m⁻² and the 80% WHC+N North Wyke soils had fluxes of 382 ± 3400 CO₂-C m⁻² (Figure 3a). Measured apparent negative or zero CO₂ fluxes are considered to be due to analytical constraints near the detection limit of the GC.

3.2.3 CH₄ fluxes

The CH₄ fluxes calculated for each sampling day provided evidence that both methanogenesis and methanotrophy were occurring simultaneously in all soils with some alternating strongly between being a source and a sink (Figure 4a,b). Calculated cumulative fluxes can be assumed to reflect the

dominant process in each soil and treatment combination. Cumulative CH₄ fluxes were highly variable within arable soils (Figure 4a).

3.3 Mineral N concentrations

For all soils there were large differences between initial untreated pre-incubation soil NO₃⁻-N contents, but not corresponding NH₄⁺-N contents (Figure 5). Unfertilised and AN fertilised post-incubation Hillsborough and North Wyke grassland soils exhibited greatest loss or microbial transformation of native soil NO₃⁻-N and added fertiliser NO₃⁻-N. Results for the unfertilised post-incubation Crichton grassland soils suggest net production of NH₄⁺-N via OM mineralisation.

Fertilisation with AN had a significant effect on NO₃⁻-N and NH₄⁺-N contents for both grassland and arable soils ($p < 0.001$) with increases of 5 (50% WHC) and 25 (80% WHC) times relative to unfertilised soils being observed.

3.4 Bivariate Correlations

Pre-incubation NO₃⁻-N contents were positively correlated with OC, TN and pre-incubation NH₄⁺-N contents and negatively correlated with soil pH. Soil TN and pH were positively correlated with clay content and C:N ratio was negatively correlated with clay content (Table 3). Soil C:N ratio was correlated positively with pH and C:N, OC and TN contents were all positively correlated to each other.

3.5 General Linear Modelling

Results from both full and reduced models are shown for arable (Table 4) and grassland (Table 5) soils. For all models, except for the arable cumulative CO₂ flux, the full model explained 1–2% more of the variation than the reduced model. For arable cumulative N₂O fluxes, the reduced model explained 60% of the variation with significant positive correlations with OC ($p < 0.01$) and NO₃⁻-N ($p < 0.05$) contents, and negative correlation with clay contents ($p < 0.01$). For grassland cumulative N₂O fluxes the reduced model explained 69% of the variation with significant negative correlations

with NO_3^- -N ($p < 0.01$) and clay ($p < 0.01$) contents and positive correlation with NH_4^+ -N ($p < 0.01$) contents.

The negative correlation between N_2O flux and clay content seems to be atypical and is caused by the high emissions and low clay contents of the two Scottish soils (Gilchriston and Crichton). When these two soils were removed from the analysis the relationship became positive.

It was not possible to adequately describe the variation of cumulative CO_2 fluxes from the arable soils with the measured variables. CO_2 fluxes from arable soils were much more variable from day to day than from grassland soils. The full model described only 2% of the variation. The reduced models explained 52% of the variation for cumulative CO_2 fluxes from the grassland soils. Cumulative CO_2 fluxes had significant ($p < 0.01$) positive correlations with NH_4^+ -N and clay contents and significant negative correlation with NO_3^- -N contents.

The reduced model for arable cumulative CH_4 fluxes explained 37% of the variation with significantly positive correlations with TN contents ($p < 0.01$) and % WHC ($p < 0.05$), and negative correlation with clay contents ($p < 0.001$). The reduced model for grassland cumulative CH_4 fluxes explained 18% of the variation with a significant positive correlation with OC contents ($p < 0.01$).

4 Discussion

4.1 N_2O fluxes and emission factors

In this study, all soils were processed and incubated in the same way but the two Scottish soils displayed substantially higher N_2O fluxes than the other soils, particularly at the higher moisture content. However, laboratory and field studies investigating the soils from these sites have reported varying results. McGeough *et al* (2016) found much higher N_2O emissions from the Scottish grassland soil studied here (60% WFPS, incubated at 15 °C for 60 days, 100 $\mu\text{g N g}^{-1}$ dry soil), although not from the Scottish arable soil. In field trials, Bell *et al* (2015b) found that the annual EF for the Scottish arable soil was ~3 to 5 times higher than grassland sites elsewhere in the UK. However, Cardenas *et al* (2019) did not observe higher annual EFs from the Scottish grassland site in

field measurements when compared to other UK grassland sites across a range of N application rates (80 - 400 kg N ha⁻¹).

In these controlled incubations, clay, mineral N and OC contents were found to be the most important factors in determining N₂O fluxes from arable and grassland soils. Clay content (and therefore texture) has frequently been identified as an important factor controlling soil N₂O emissions (Skiba and Ball, 2002; Dobbie and Smith, 2003; Stehfest and Bouwmann, 2006). Positive correlations between N₂O flux and OC content have also previously been observed (Stehfest and Bouwmann, 2006).

In this study, EFs were consistently below the value assumed in the IPCC Tier 1 methodology (1%) (IPCC, 2006a). It should be noted that the 22 day incubation period used in this study was much shorter than the 12 months normally used to assess EFs, however, it does provide a valuable ranking of the proportion of emissions that can be attributed to the added N source.

Field experiments at the Scottish sites have also reported low EFs in the short term after AN application. Hinton *et al* (2015) found EFs from 0.44–0.56% for the five weeks following AN application, but annual EFs of 1.36, 0.96 and 1.08% for AN application rates of 120, 160 and 200 kg N ha⁻¹ at the Scottish arable site. Smith *et al* (2012) found an EF of 0.61% (over the growing season) at the Scottish grassland site in 2004, however, the EF in 2003 was higher (1.13%). EFs are highly variable, values between 0.2 and 7% have been reported for agricultural fields in Scotland (Clayton *et al*, 1997; Smith *et al*, 1998; Dobbie *et al*, 1999) and the range of uncertainty associated with the IPCC default value is 0.3–3.0% (IPCC, 2006b).

It has been suggested that the higher EFs from Scottish sites is due to the incidence and intensity of rainfall (and therefore WFPS) at the time of fertiliser application (Dobbie *et al*, 1999). However, this does not explain the higher EFs from Scottish soils under controlled conditions. Soil OC stocks are higher in Scottish agricultural soils (compared with elsewhere in the UK) (Bradley *et al*, 2005) and so the distribution and availability of soil OC pools may differ. Further investigation of OC pools and

their availability, aggregate-stabilising minerals and microbial communities within the UK soils studied here may explain these unexpected findings.

4.2 CO₂ fluxes from UK arable and grassland agricultural soils

A positive correlation between grassland CO₂ fluxes and clay content was found in this study, which is counter to the theory that higher clay contents provide a greater opportunity for chemical protection of OM by adsorption. Dilustro *et al* (2005) also observed greater CO₂ fluxes from clay textured (> 19% clay) than sandy textured (< 12% clay) forest soils. However, they attribute this to a more dense vegetation (and so greater root respiration) on the clay soils and the sandy soils being excessively drained for part of the study period.

In this study, grassland soil CO₂ flux showed a positive correlation with NH₄⁺-N content and a negative correlation with NO₃⁻-N content. However, fertilisation with AN was observed to decrease or have no effect on CO₂ emissions. Zaman *et al* (2002) speculate that fertilisation without the addition of C cannot drive increased microbial growth or respiration. There are several conflicting results in the literature which show increases (Baggs *et al*, 2003), decreases (al-Kaisi *et al*, 2008) and no effect (Baggs *et al*, 2003; Garcia-Ruiz and Baggs, 2007 and al-Kaisi *et al*, 2008) of AN fertilisation on CO₂ flux.

4.3 CH₄ fluxes from UK arable and grassland agricultural soils

Individual soils showed highly variable CH₄ fluxes throughout the incubation period, the oscillation of fluxes from net source to net sink indicates that methanogenesis and methanotrophy were occurring simultaneously (Ekberg and Christensen, 2006). As a result the net emissions of CH₄ when expressed as CO_{2e} was small relative to the other greenhouse gases. Soil moisture content, native N content and clay content explained significant variation in emissions from arable soils and OC content from grassland soils.

Soils with coarse textures have higher oxidation rates of CH₄ than more fine textured soils, attributable to low porosity and high water retention in fine textured soils causing low gas diffusivity into the soil (Dörr *et al*, 1993; Dutaur and Verchot, 2007; Tate *et al*, 2007).

In this study increasing the moisture content from 50 to 80% WHC actually reduced emissions (increased sinks) in all cases except one. It is possible that the methanotrophic microbial population was under water stress at the lower WHC level. von Fischer *et al* (2009) found that methanotrophic activity dropped off sharply below 40% WFPS in a sandy loam grassland soil. The presence of NO_3^- -N would also act as an inhibitor to methanotrophs as this would be used in preference to organic carbon as a terminal electron acceptor.

4.4 Overall GHG budget

When expressing the GHG fluxes measured from incubated soils in this study in terms of their GWPs, it is clear that the GHG budget is driven by N_2O and CO_2 fluxes. However, under field conditions much of the CO_2 released from soil by respiration is returned by photosynthesis and so may not be a net source of atmospheric CO_2 . This highlights the importance of accurately assessing the effects of agricultural soil management on N_2O emissions (Gao *et al.* 2018).

Conclusions

Generally, the results were in support of those found in the literature for a wide range of soils, conditions and locations with soil texture, soil mineral N and OC contents found to be the most important measured variables controlling GHG fluxes. However, the N_2O emissions from Scottish soils were more sensitive to ammonium nitrate fertilisation, particularly at 80% WHC, than the other UK agricultural soils studied here. The reason for the high EFs from Scottish soils remains unclear, however, it is possible that it could be linked to differences in the structure of the microbial population or composition of the soil organic matter pools. Resolving this issue would be valuable in making more precise predictions of N_2O emissions in response to soil management.

Acknowledgements

We would like to thank the Scottish Governments Rural Affairs Food and the Environment Strategic Research and DEFRA for funding. We would also like to thank the site managers from ADAS, AFBI and Rothamsted Research study sites for providing soil.

References

- al-Kaisi, M.M., Kruse, M.L. and Sawyer, J.E. (2008) Effect of nitrogen fertilizer application on growing season soil carbon dioxide emission in a corn-soybean rotation. *Journal of Environmental Quality* 37:325–332
- Baggs, E.M., Stevenson, M.P., Pihlatie, M., Regar, A., Cook, H. and Cadisch, G. (2003) Nitrous oxide emissions following application of residues and fertiliser under zero and conventional tillage. *Plant and Soil* 254:361–370
- Ball, B.C. (2013) Soil structure and greenhouse gas emissions: a synthesis of 20 years of experimentation. *European Journal of Soil Science* 64:357–373
- Bell, M.J., Rees, R.M., Cloy, J.M., Topp, C.F.E., Bagnall, A. and Chadwick, D.R. (2015a) Nitrous oxide emissions from cattle excreta applied to a Scottish grassland: Effects of soil and climatic conditions and a nitrification inhibitor. *Science of the Total Environment* 508:343-353
- Bell, M.J., Hinton, N., Cloy, J.M., Topp, C.F.E., Rees, R.M., Cardenas, L., Scott, T., Webster, C., Ashton, R.W., Whitmore, A.P., Williams, J.R., Balshaw, H., Paine, F., Goulding, K.W.T. and Chadwick, D.R. (2015b) Nitrous oxide emissions from fertilised UK arable soils: Fluxes, emission factors and mitigation. *Agriculture, Ecosystems & Environment* 212, 134-147.
- Bell M.J., Cloy J.M., Topp C.F.E., Ball B.C., Bagnall A., Rees R.M., Chadwick D.R., (2016) Quantifying N₂O emissions from intensive grassland production: the role of synthetic fertiliser type, application rate, timing, and nitrification inhibitors, *Journal of Agricultural Science* doi.org/10.1017/S0021859615000945
- Bradley, R.I., Milne, R., Bell, J., Lilly, A., Jordan, C. and Higgins, A. (2005) A soil carbon and land use database for the United Kingdom. *Soil Use and Management* 21:363-369
- Cardenas, L.M., Bhogal, A., Chadwick, D.R., McGeough, K., Misselbrook, T., Rees, R.M., Thorman, R.E., Watson, C.J., Williams, J.R., Smith, K.A. & Calvet, S (2019) Nitrogen use efficiency and nitrous oxide emissions from five UK fertilised grasslands. *Science of the Total Environment* 661:696-710

321 Clayton, H., McTaggart, I.P., Parker, J., Swan, L. and Smith, K.A. (1997) Nitrous oxide emissions
 322 from fertilised grassland: a 2-year study of the effects of N fertiliser form and environmental
 323 conditions. *Biology and Fertility of Soils* 25:252–260

324 Cloy, J.M. and Smith, K.A. (2015) Greenhouse Gas Emissions. *In: Reference Module in Earth*
 325 *Systems and Environmental Sciences* Online reference database, Elsevier, Oxford.

326 Dilustro, J.J., Collins, B., Duncan, L. and Crawford, C. (2005) Moisture and soil texture effects on
 327 soil CO₂ efflux components in southeastern mixed pine forests. *Forest Ecology and Management*
 328 204:85–95

329 Dobbie, K.E., McTaggart, I.P. and Smith, K.A. (1999) Nitrous oxide emissions from intensive
 330 agricultural systems: Variation between crops and seasons, key driving variables, and mean emission
 331 factors. *Journal of Geophysical Research* 104:26891–26899

332 Dobbie, K.E. and Smith, K.A. (2003) Nitrous oxide emission factors for agricultural soils in Great
 333 Britain: the impact of soil water-filled pore space and other controlling factors. *Global Change*
 334 *Biology* 9:204–218

335 Dörr, H., Katruff, L. and Levin, I. (1993) Soil texture parameterization of the methane uptake in
 336 aerated soils. *Chemosphere* 26:697–713

337 Dutaur, L. and Verchot, L.V. (2007) A global inventory of the soil CH₄ sink. *Global Biogeochemistry*
 338 *Cycles* 21 doi: 10.1029/2006GB002734

339 Ekberg, A. and Christensen, T.R. (2006) Wetlands and methane emission. *In* Encyclopaedia of Soil
 340 Science, Second Edition. Ed. Lal, R. New York, USA.

341 Gao, B., Huang, T., Ju, X., Gu, B., Huang, W., Xu, L., Rees, R.M., Powlson, D.S., Smith, P. & Cui, S. 2018.
 342 Chinese cropping systems are a net source of greenhouse gases despite soil carbon sequestration.
 343 *Global Change Biology*, **24**, 5590-5606.

344 Garcia-Ruiz, R. and Baggs, E.M. (2007) N₂O emission from soil following combined application of
 345 fertiliser-N and ground weed residues. *Plant Soil* 299:263–274

346 Hinton, N.J., Cloy, J.M., Bell, M.J., Chadwick, D.R., Topp, C.F.E. and Rees, R.M. (2015) Managing
 347 fertiliser nitrogen to reduce nitrous oxide emissions and emission intensities from a cultivated
 348 Cambisol in Scotland. *Geoderma Regional* 4:55–65

349 Howard, D.M. and Howard, P.J.A. (1993) Relationships between CO₂ evolution, moisture content and
 350 temperature for a range of soil types. *Soil Biology and Biochemistry* 25:1537–1546

351 Inselsbacher, E., Wanek, W., Ripka, K., Hackl, E., Sessitsch, A., Strauss, J. and Zechmeister-
 352 Boltenstern, S. (2011) Greenhouse gas fluxes respond to different N fertilizer types due to altered
 353 plant-soil-microbe interactions. *Plant Soil* 343:17–35

354 IPCC (Intergovernmental Panel on Climate Change) (2006a) 2006 IPCC Guidelines for national
 355 greenhouse gas inventories. IGES, Japan

356 IPCC (Intergovernmental Panel on Climate Change) (2006b) N₂O emissions from managed soils, and
 357 CO₂ emissions from lime and urea application. Chapter 11. Agriculture, Forestry and other land use.
 358 vol. 4. IPCC Guidelines for National Greenhouse Gas Inventories

359 IPCC (Intergovernmental Panel on Climate Change) (2014) Climate Change 2014: Synthesis Report.
 360 Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental
 361 Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva,
 362 Switzerland

363 Malik, A.A., Puissant, J., Buckeridge, K.M., Goodall, T., Jehmlich, N., Chowdhury, S., Soon Gweon,
 364 H., Peyton, J.M., Mason, K.E., van Agtmaal, M., Bland, A., Clark, I.M., Whitaker, J., Pywell, R.F.,
 365 Ostle, N., Gleixner, G. and Griffiths, R.I. (2018) Land use driven change in soil pH affects microbial
 366 carbon cycling processes. *Nature Communications* 9:3591

367 McGeough, K.L., Watson, C.J., Müller, C., Laughlin, R.J. and Chadwick, D.R. (2016) Evidence that
 368 the efficacy of the nitrification inhibitor dicyandiamide (DCD) is affected by soil properties in UK
 369 soils. *Soil Biology and Biochemistry* 94:222-232

370 Norton, J.M. and Firestone, M.K. (1996) N dynamics in the rhizosphere of *Pinus Ponderosa*
 371 seedlings. *Soil Biology & Biochemistry* 28:351–362

372 Saggar, S., Tate, K.R., Giltrap, D.L. and Singh, J. (2008) Soil-atmosphere exchange of nitrous oxide
 373 and methane in New Zealand terrestrial ecosystems and their mitigation options: a review. *Plant Soil*
 374 309:25–42

375 Schrumpf, M., Kaiser, K., Guggenberger, G., Persson, T., Kögel-Knabner, I. and Schulze, E.D. (2013)
 376 Storage and stability of organic carbon in soils as related to depth, occlusion within aggregates, and
 377 attachment to minerals. *Biogeosciences* 10:1675–1691

378 Shepherd, T.G. (2009) Visual Soil Assessment. Volume 1. *Field guide for pastoral grazing and*
 379 *cropping on flat rolling country*. 2nd Edition, Horizons Regional Council, Palmerston North, New
 380 Zealand, pp. 119.

381 Singh, U., Sanabria, J., Auston, E.R. and Agyin-Birikorang, S. (2011) Nitrogen transformation,
 382 ammonia volatilization loss, and nitrate leaching in organically enhanced nitrogen fertilizers relative
 383 to urea. *Soil Science Society of America Journal* 76:1842–1854

384 Skiba, U. and Ball, B. (2002) The effect of soil texture and soil drainage on emissions of nitric oxide
 385 and nitrous oxide. *Soil Use and Management* 18:56–60

386 Smith, K.A., McTaggart, I.P., Dobbie, K.E. and Conen, F. (1998) Emissions of N₂O from Scottish
 387 agricultural soils, as a function of fertilizer N. *Nutrient Cycling in Agroecosystems* 52:123–130

388 Smith K.A., Ball, T., Conen, F., Dobbie, K.E., Massheder, J. and Rey, A. (2003) Exchange of
 389 greenhouse gases between soil and atmosphere: interactions of soil physical factors and biological
 390 processes. *European Journal of Soil Science* 54:79–791

391 Smith, K.A., Dobbie, K.E. Thorman, R., Watson, C.J., Chadwick, D.R., Yamulki, S. and Ball, B.C.
 392 (2012) The effect of N fertilizer forms on nitrous oxide emissions from UK arable land and grassland.
 393 *Nutrient Cycling and Agroecosystems* 93:127–149

394 Stehfest, E. and Bouwman, L. (2006) N₂O and NO emission from agricultural fields and soils under
 395 natural vegetation: summarizing available measurement data and modelling of global annual
 396 emissions. *Nutrient Cycling in Agroecosystems* 74:207–228

397 Tate, K.R., Ross, D.J., Saggar, S., Hedley, C.B., Dando, J., Singh, B.K. and Lambie, S.M. (2007)
 398 Methane uptake in soils from *Pinus radiata* plantations, a reverting shrubland and adjacent pastures:
 399 Effects of land-use change, and soil texture, water and mineral nitrogen. *Soil Biology & Biochemistry*
 400 39:1437–1449

401 Von Fischer, J.C., Butters, G., Duchateau, P.C., Thelwell, R.J. and Siller, R. (2009) In situ measures
 402 of methanotroph activity in upland soils: A reaction-diffusion model and field observation of water
 403 stress. *Journal of Geophysical Research* 114: doi: 10.1029/2008JG000731

404 Zaman, M., Cameron, K.C., Di, H.J. and Inubushi, K. (2002) Changes in mineral N, microbial
 405 biomass and enzyme activities in different soil depths after surface applications of dairy shed effluent
 406 and chemical fertilizer. *Nutrient Cycling in Agroecosystems* 63:275–290

Table 1

Land Use	Site	Average annual temp. (°C)	Soil texture	Annual rainfall (mm)	100% WHC (g water g ⁻¹ soil)	TN (g N kg ⁻¹ soil)	OC (g C kg ⁻¹ soil)	C:N ratio	Clay (% by weight)	pH
Grassland	Crichton	10.2	Sandy loam	> 950	0.55 (0.03)	3.06 (0.163)	32.6 (1.52)	10.68 (0.046)	12.5	5.3 (0.03)
	Drayton	10.3	Clay	0 - 750	0.51 (0.04)	4.62 (1.383)	50.8 (15.60)	11.01 (0.477)	50.1	6.6 (0.42)
	Hillsborough	9.8	Clay loam	751 - 950	0.34 (0.04)	7.72 (0.107)	12.4 (0.77)	15.99 (0.077)	28.1	5.9 (0.03)
	North Wyke	9.6	Silty clay	> 950	0.64 (0.03)	2.72 (0.060)	22.2 (0.83)	8.17 (0.089)	32.5	4.5 (0.02)
	Pwllpeiran	9.3	Clay loam	> 950	0.70 (0.16)	4.41 (0.638)	41.8 (6.06)	9.49 (0.035)	23.8	5.1 (0.10)
Arable	Gilchriston	8.7	Sandy Clay loam	< 750	0.45 (0.02)	0.93 (0.023)	12.7 (0.53)	13.57 (0.213)	12.7	5.9 (0.03)
	Woburn	10.9	Loamy sand	< 750	0.45 (0.04)	0.86 (0.037)	9.4 (0.40)	10.93 (0.027)	10	7.0 (0.08)
	Rosemaund	10.4	Clay loam	751 - 950	0.30 (0.05)	1.28 (0.062)	10.5 (0.18)	8.21 (0.163)	20.9	5.1 (0.02)
	Boxworth	9.7	Clay	550	0.51 (0.00)	1.85 (0.043)	19.0 (0.35)	10.27 (0.036)	44.8	7.9 (0.05)

Table 2

Treatment	Land Use	Site	N ₂ O	CO ₂	CH ₄
50% WHC	Arable	Boxworth	651	1460	10.97
		Gilchriston	477	985	4.07
		Rosemaund	-41.0	301	12.25
		Woburn	21.1	-90.6	5.95
	Grassland	Crichton	884	2760	-0.82
		Drayton	298	2040	-33.28
		Hillsborough	-61.4	140	33.34
		North Wyke	128	1060	-0.41
		Pwllpeiran	99.9	-168	-6.69
		50% WHC+N	Arable	Boxworth	394
Gilchriston	570			1740	4.58
Rosemaund	-49.1			2770	32.18
Woburn	-2.8			1840	0.35
Grassland	Crichton		495	2750	-21.1
	Drayton		331	3720	10.38
	Hillsborough		-8.4	945	21.87
	North Wyke		169	1990	-4.07
	Pwllpeiran		-13.9	-263	17.29
	80% WHC		Arable	Boxworth	463
Gilchriston		1450		1440	-7.1
Rosemaund		-81.8		1980	5.28
Woburn		75.3		363	-26.06
Grassland		Crichton	1300	4780	-19.66
		Drayton	411	8890	-8.64
		Hillsborough	109	2550	26.71
		North Wyke	297	3390	-1.35
		Pwllpeiran	41.6	437	-21.29
		80% WHC+N	Arable	Boxworth	1436
Gilchriston	12300			1220	-6.43
Rosemaund	-56.9			891	38.04
Woburn	114			-69.9	-20.11
Grassland	Crichton		182000	1780	-20.12
	Drayton		1840	6390	1.54
	Hillsborough		127	3810	12.57
	North Wyke		1230	382	-13.4
	Pwllpeiran		74.5	938	-2.71

Table 3

Variate	Clay (% by weight)	OC (% by weight)	TN (% by weight)	C:N ratio	pH	NH ₄ ⁺ -N (mg kg ⁻¹)	NO ₃ ⁻ -N (mg kg ⁻¹)
clay	1.00						
OC	0.19	1.00					
TN	0.33 *	0.96 *	1.00				
C:N	-0.21 *	0.69 *	0.51 *	1.00			
pH	0.26 *	-0.06	-0.16	0.27 *	1.00		
NH ₄ ⁺ -N	0.00	0.02	0.01	0.01	0.02	1.00	
NO ₃ ⁻ -N	0.09	0.27 *	0.31 *	0.00	-0.23 *	0.89 *	1.00

Table 4

Variable	Arable CO ₂				Arable N ₂ O				Arable CH ₄			
	Full Model		Reduced Model		Full Model		Reduced Model		Full Model		Reduced Model	
	CV	SE	CV	SE	CV	SE	CV	SE	CV	SE	CV	SE
NO ₃ N content	-1732	4.33			0.00048	0.000671	0.0003 ****	0.0000				
NH ₄ ⁺ -N content	-2.43	4.36			-0.000178	0.000684			-0.0003	0.0002		
% WHC	19	15.4			0.0061	0.0032			0.0146 ****	0.0065	0.0146 ****	0.0066
OC content	3024	2535	1082	604	2.798 *	0.486	2.723 *	0.328				
TN content	-19479	23840							94.4 **	28.2	72.9 *	18.5
C:N ratio									0.0851	0.0827		
Clay content					-0.0658 *	0.013	-0.0638 *	0.0089	-0.243 **	0.078	-0.1855 *	0.0535
pH												
Constant	-1732	1458	-392	818	-2.361 *	0.454	-1.774	0.259	-7.73 **	2.56	-5.59 *	1.2
F	p = 0.328		p = 0.08		*		*		*		*	
R ²	0.02		0.05		0.61		0.60		0.39		0.37	

Table 5

Variable	Grassland CO ₂				Grassland N ₂ O				Grassland CH ₄			
	Full Model		Reduced Model		Full Model		Reduced Model		Full Model		Reduced Model	
	CV	SE	CV	SE	CV	SE	CV	SE	CV	SE	CV	SE
NO ₃ N content	7.32	8.73	-6.26 *	1.24	-0.0022 **	0.0007	-0.0018 *	0.0002	0.0030	0.0035		
NH ₄ ⁺ -N content	-4.46	8.86	9.32 *	1.41	0.0028 *	0.0007	0.0023 *	0.0002	-0.0033	0.0035		
% WHC	8.8	17.1			0.003	0.0024			0.0120	0.0067		
OC content					-0.094	0.114			0.008	0.437	0.1036 *	0.0279
TN content	-39464	24582			2.26	3			-8.08	8.96		
C:N ratio	2108	1239							0.549	0.608		
Clay content	113.9 *	33.6	88.7 *	19.5	-0.00537	0.00427	-0.008 **	0.0028				
pH	2127	1458			-0.206	0.206			0.253	0.564		
Constant	-22114	12672	526	818	1.466	0.608	0.7506*	0.0806	-5.36	5.99	-0.509 **	0.184
F	*		*		*		*		***		*	
R ²	0.54		0.52		0.70		0.69		0.20		0.18	

Table 1: Land use, average annual temperature (°C), soil texture, annual average precipitation for the nine soils, pre-incubation average 100% water holding capacity (WHC), total nitrogen (N) and, organic carbon (OC) contents, C:N ratios, clay contents and pH for the grassland and arable agricultural soils.

Table 2: Global warming potentials (CO₂-eq) of grassland and arable soils incubated over a 22 day period at 50 or 80% water holding capacity (WHC) and with or without ammonium nitrate (N) fertiliser.

Table 3: Bivariate correlations between measured soil properties (pre-treatment) for all nine soils. Clay, organic carbon (OC), total nitrogen (TN) NH₄⁺-N and NO₃⁻-N contents, pH and C:N ratio. * Significant correlations ($p < 0.05$).

Table 4: Full and reduced multiple linear regression models for arable soils. Variables assessed were NO₃⁻-N and NH₄⁺-N contents (mg kg⁻¹), % water holding capacity (WHC), organic carbon (OC) and total nitrogen contents (TN) (% by weight), C:N ratios, clay content (% by weight) and pH. CV is the coefficient of variance, SE is the standard error. Significance levels are denoted as follows: * $p < 0.001$, ** $p < 0.005$, *** $p < 0.01$, **** $p < 0.05$.

Table 5: Full and reduced multiple linear regression models for grassland soils. Variables assessed were NO₃⁻-N and NH₄⁺-N contents (mg kg⁻¹), % water holding capacity (WHC), organic carbon (OC) and total nitrogen (TN) contents (% by weight), C:N ratios, clay content (% by weight) and pH. CV is the coefficient of variance, SE is the standard error. Significance levels are denoted as follows: * $p < 0.001$, ** $p < 0.005$, *** $p < 0.01$, **** $p < 0.05$.

Figure 1: Cumulative N₂O fluxes (mg N₂O-N m⁻²) from a) arable and b) grassland soils for 50% water holding capacity (WHC) (50%), ammonium nitrate fertilised 50% WHC (50%+N), 80% WHC (80%) and ammonium nitrate fertilised 80% WHC (80%+N) treatments over a 22 day incubation period. Two-way ANOVA. * p < 0.001, ** p < 0.005, *** p < 0.05.

Figure 2: Emission factors (%) for N₂O emissions from ammonium nitrate fertilised soils (70 kg N ha⁻¹): a) arable soils at 50% and 80% WHC (water holding capacity), b) grassland soils at 50% and 80% WHC. B = Boxworth, G = Gilchriston, R = Rosemaund, W = Woburn, C = Crichton, D = Drayton, Hillsborough = H, N = North Wyke, P = Pwllpeiran.

Figure 3: Cumulative CO₂ fluxes (mg CO₂-C m⁻²) for a) arable and b) grassland soils for 50% water holding capacity (WHC) (50%), ammonium nitrate fertilised 50% WHC (50%+N), 80% WHC (80%) and ammonium nitrate fertilised 80% WHC (80%+N) treatments over a 22 day incubation period. Measured apparent negative or zero CO₂ fluxes are considered to be due to analytical constraints near the detection limit of the GC.

Figure 4: Cumulative CH₄ fluxes (mg CH₄-C m⁻²) for a) arable and b) grassland soils for 50% water holding capacity (WHC) (50%), ammonium nitrate fertilised 50% WHC (50%+N), 80% WHC (80%) and ammonium nitrate fertilised 80% WHC (80%+N) treatments over a 22 day incubation period.

Figure 5: a) Arable soil NO₃⁻-N, b) grassland soil NO₃⁻-N, c) arable soil NH₄⁺-N and d) grassland soil NH₄⁺-N contents for untreated pre-incubation (Pre-inc) soils and 50% WHC (50%), ammonium nitrate fertilised 50% WHC (50%+N), 80% WHC (80%) and ammonium nitrate fertilised 80% WHC (80%+N) post-incubation soils. Bars with different letters are significantly different. B = Boxworth, G = Gilchriston, R = Rosemaund, W = Woburn, C = Crichton, D = Drayton, Hillsborough = H, N = North Wyke, P = Pwllpeiran.

Figure 1a)

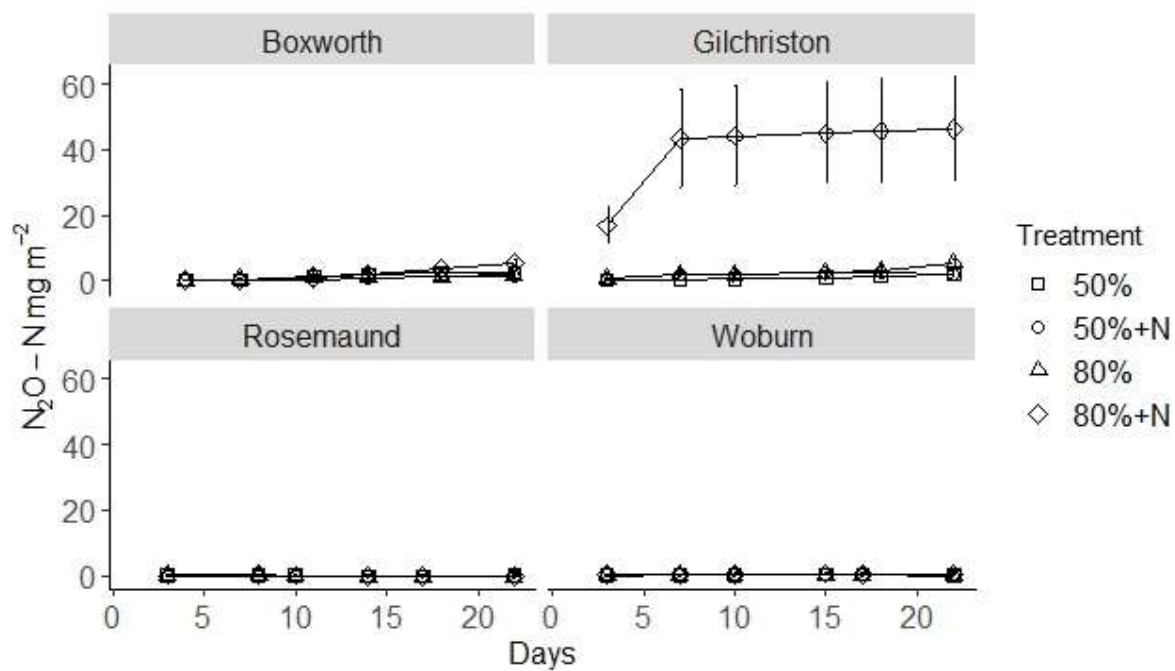


Figure 1b)

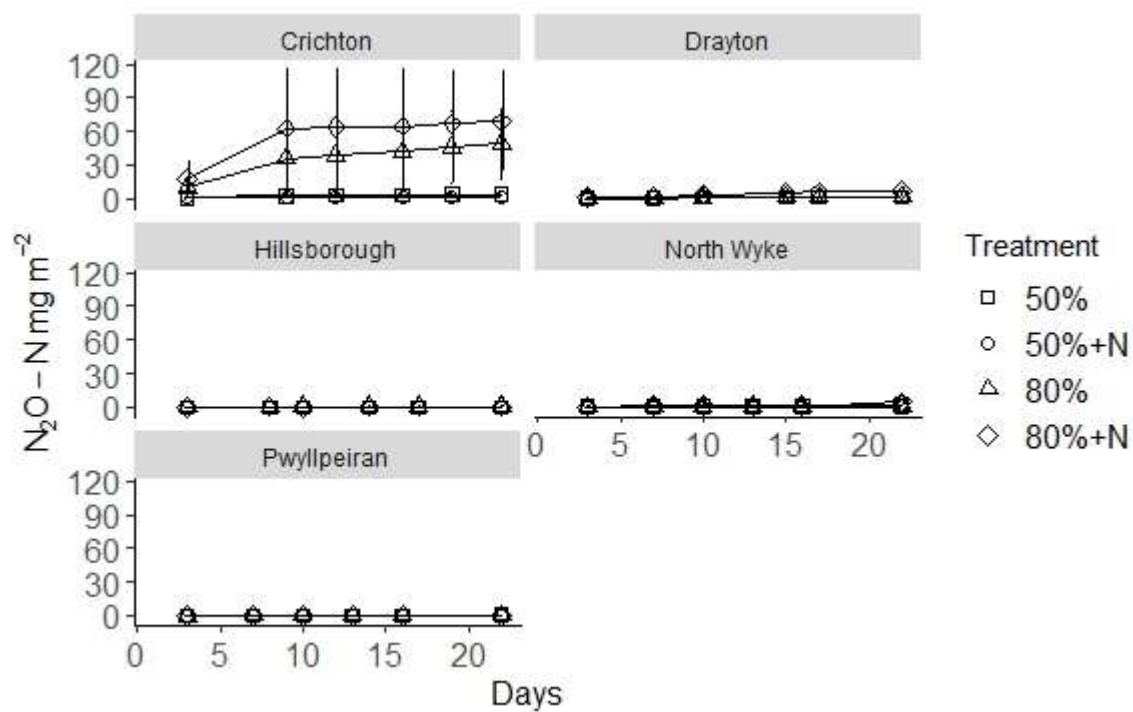


Figure 2)

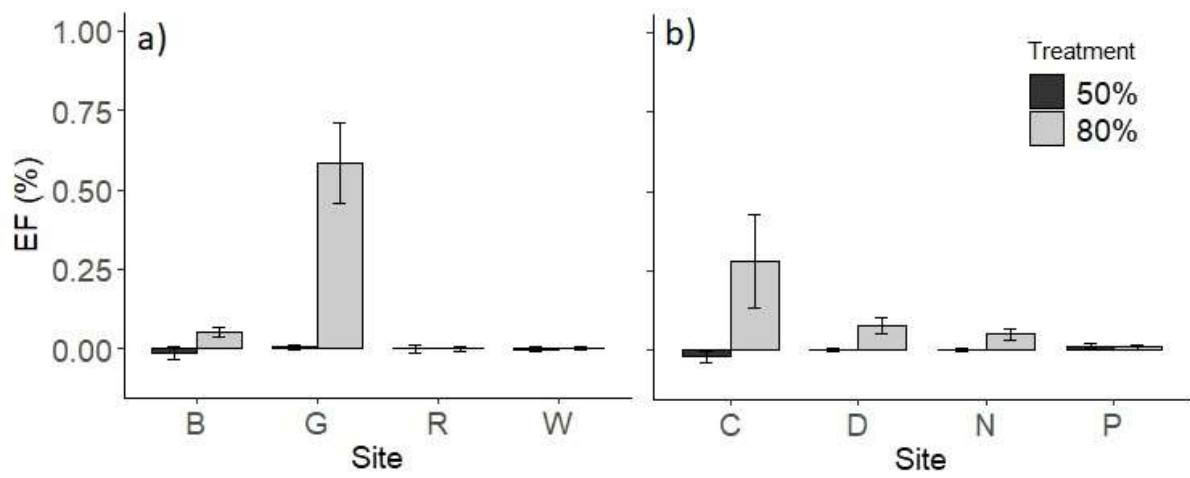


Figure 3a)

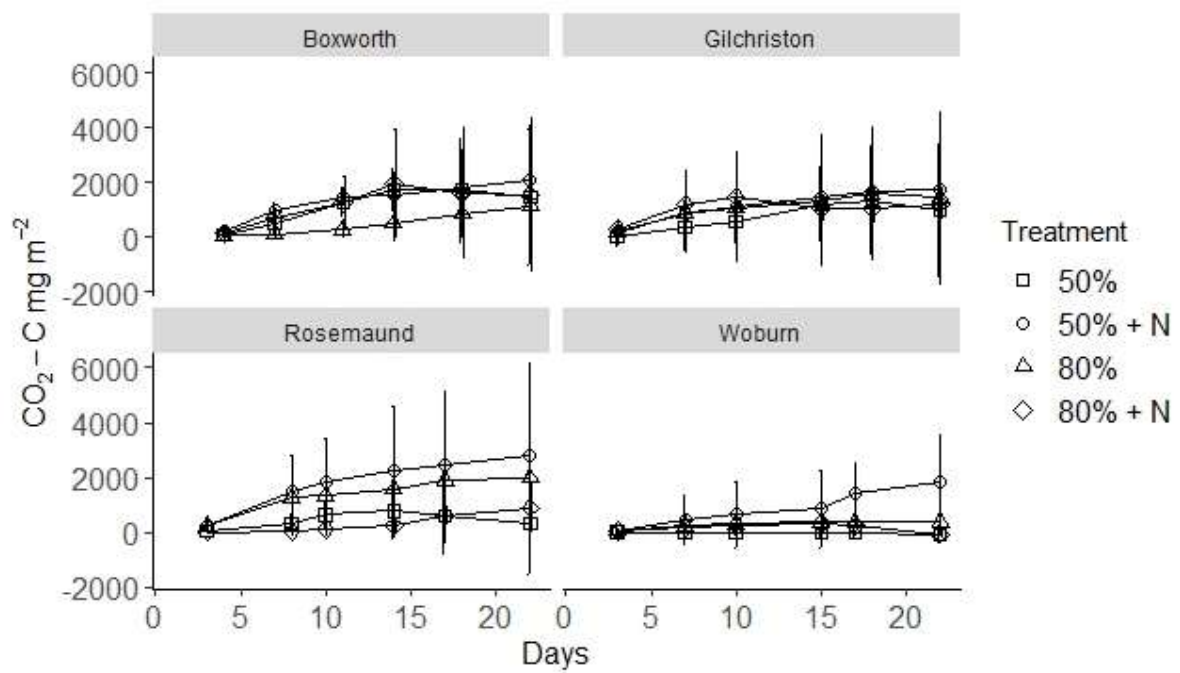


Figure 3b)

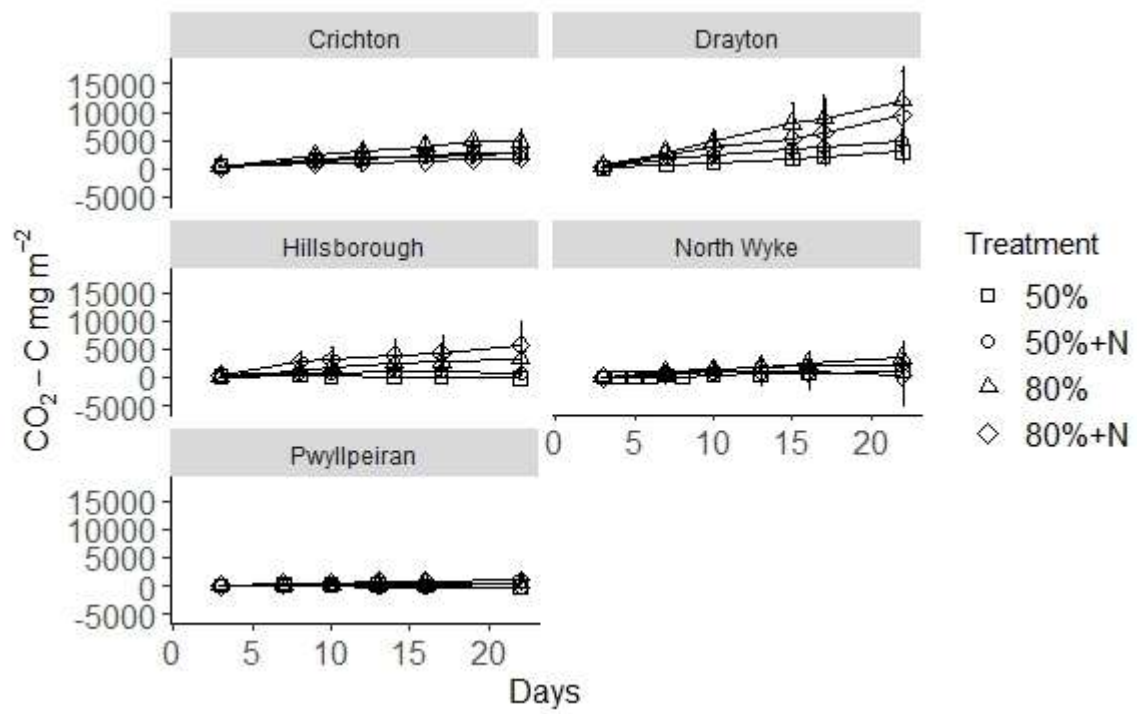


Figure 4a)

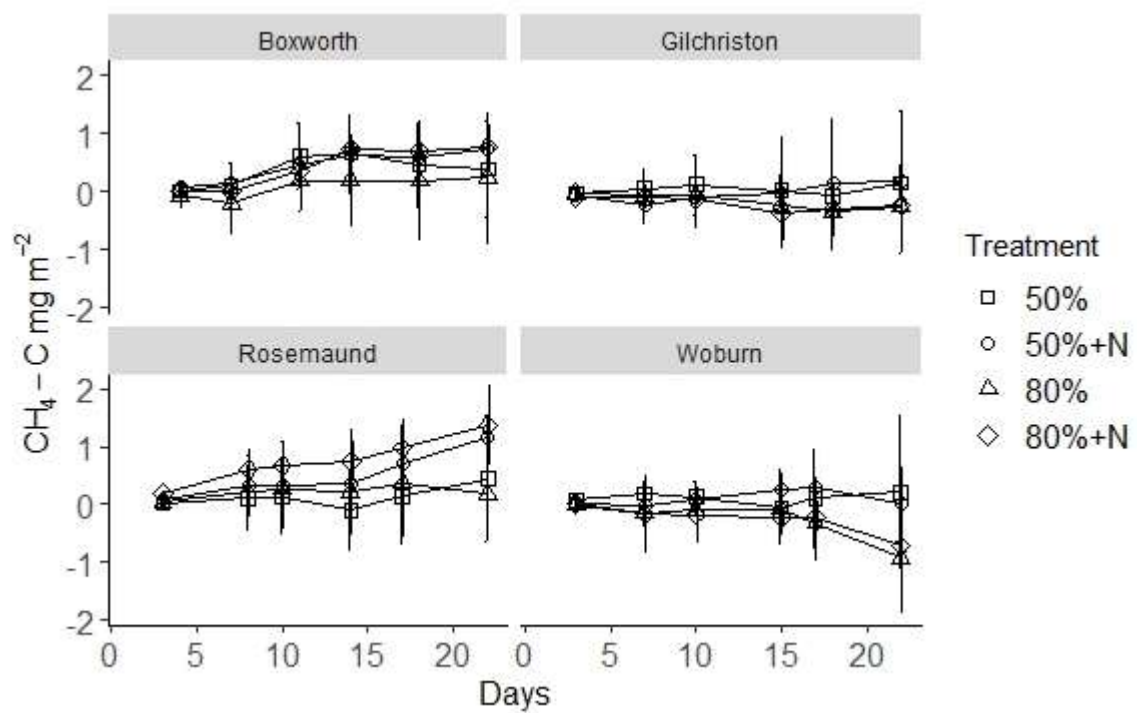


Figure 4b)

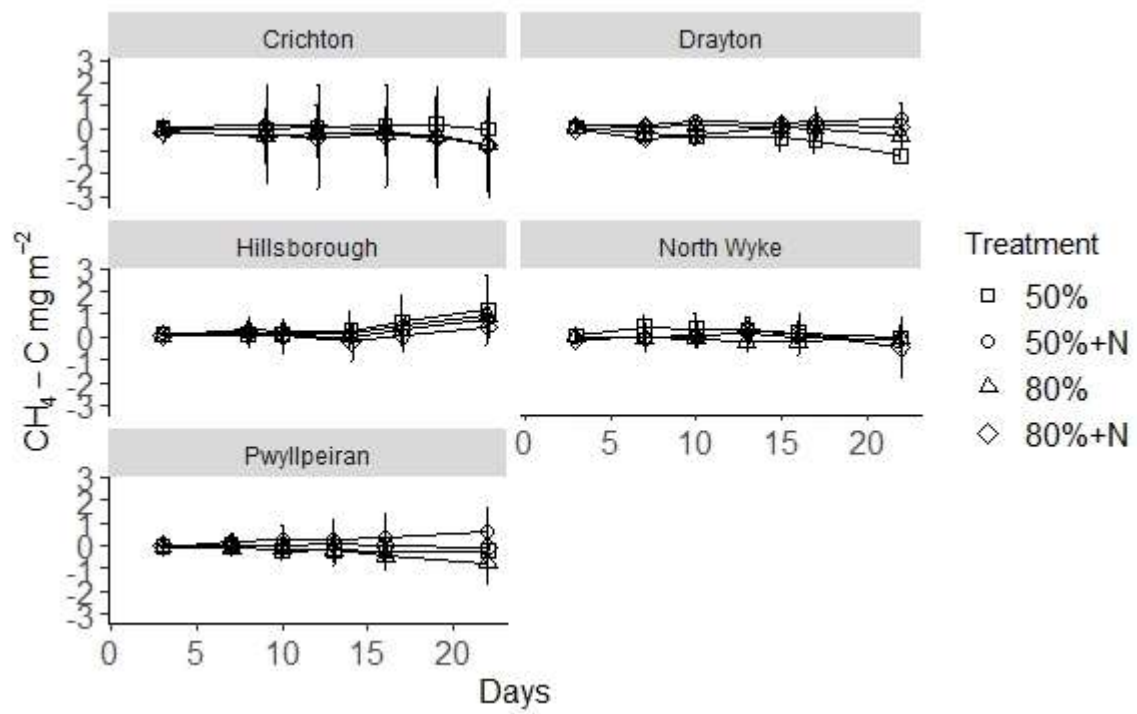


Figure 5)

